Fabrication and characterization of solid-state, conducting polymer actuators

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ABSTRACT

We report here the fabrication and characterization of solid-state, conducting polymer actuators. The electrochemical activity of polyaniline (PANI) thin film coated with solid-state polyelectrolyte is very similar to the polyaniline thin film in an aqueous solution. The solid-state actuator is adhere to a lever arm of an force transducer and the force generation is measured in real time. The force generated by the actuator is found to be length dependent. However, the overall torques generated by the actuators with different lengths remains essentially the same. The effect of stimulation signals such as voltage, current, on the bending angle and displacement is also studied using square wave potential.

Keyword: polyaniline, solid-state, actuator, force, bending angle

1. INTRODUCTION

Conducting polymer (CP) actuators have attracted considerable attention due to their light weight, low operating potential, high mechanical strength, and potential applications in advanced robotics, microactuators and artificial muscles[1-5]. There are mainly two types of surrounding stimuli that can trigger the movement of CP actuators: electrical and chemical. Electrical potential can promote movements in CP actuators because a volume change occurs during the electrochemical doping-dedoping process. In the past few years, research have focused on electrochemically driven CP actuators. Actuators with different configurations based on CP membranes or fibers have been fabricated that show either bending-recovery movement or linear extension.[6-13] In addition, electrochemically triggered microactuators have recently been used to handle, transport, and separate biological species.[14]

The fabrication of CP-engineered articles such as fibers and membranes has suffered from the fact that the fibers and membranes were neither soluble nor fusible. In many cases, CP thin films have been synthesized using electrochemical methods. Recent successes in the fabrication of PANI membranes and fibers from highly concentrated PANI emeraldine base (EB) solution, as well as PANI's high environmental stability, low cost, facile redox potential, and relatively high conductivity, make it one of the most promising CPs for practical application in fabricating CP actuators.[15-17] Previously, we reported the application, through doping and dedoping mechanisms, of PANI integrally skinned asymmetric membranes (PANI ISAMs) as monolithic chemical and electrochemical actuators in basic or acidic media (see Scheme 1).[18,19] It remains a major challenge to fabricate solid-state CP actuators that operate in air. As of today only some scattered reports of using CP to fabricate actuators that operate in air. The early work involve the usage of polypyrrole in a trilayer configuration in which polyelectrolyte was soaked in the central layer and serve as reservoir for electrolyte which allows the solid-state actuators to redox and bends in both directions. The linear actuator constructed by encapsulating the PANII fiber with polyelectrolyte and operate in air have also been demonstrated. Most recently, Lu et. al., report a PANI linear actuator using the solid-in-hollow fiber configuration. Ionic liquids have demonstrated their ability to significantly improve the lifetimes of conducting polymer electrochemical devices. This improvement is largely due to their unique properties of wide electrochemical windows, high conductivity, non-volatility, non-flammability, thermal stability, and a wide liquid-state range. However, most work, which has been performed in

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the liquid phase of ionic liquids, has limited the practical applications of the device. Despite all the above successes, fabrication of a CP actuator appear to be quite troublesome and did not show a lot of promises toward commercial applications.

In this paper, we put together a simple polyelectrolyte system consists of poly (vinyl alcohol), poly(vinylsulfonic acid, sodium salt), poly(aniline sulfonic acid), and poly(anetholesulfonic acid, sodium salt, Aldrich and coat it on the PANI thin film. Two platinum electrodes are later attached to both sides of the thin film as both working and counter electrodes. These as-prepared PANI actuators are fully characterized in terms of their electrochemical activity and performance characteristics. We first measure the current, bending angle and displacement as a function of time using square wave potential, which provide valuable insights in better realizing the deformation mechanism. The force generation is then measured by attached the end of the actuator to the tip of force transducer lever arm. The overall torque can then be calculated by multiply the length of the actuator with the total force generated. Our results indicate that the new polyelectrolyte system offers electrochemical activity similar to that in aqueous solution. Force generation is

2. EXPERIMENTAL SECTION

PANI emeraldine base (EB) powder (Neste Oy), N-methyl-2-pyrrolidinone (NMP) (99%, Aldrich), hexane (99%, Aldrich), and hexamethyleneimine (HXMI) (98%, Acros) were used without further purification.

A typical example of preparing a highly concentrated EB solution is stated as follows: 3.6 g of NMP are mixed with 0.4 g of HXMI. This mixture is placed inside a 10-ml Teflon® vial, then sealed, and placed inside a 60°C oven for 5 minutes. Then the vial is removed from the oven, and the EB powder (0.7 g) is added to this solution, which is stirred with a homogenizer at 5,000 rpm over a 25-minute period until it becomes homogeneous and flows freely. The mass content of EB powder in this solution is ~15% w/w. This visually uniform solution is then stirred for 1 hour using an electric stirrer. The final solution is poured onto a 12× 20 cm glass substrate and a wet film is prepared by using a Gardner blade with a preset thickness of 8—10 mil. This wet film is then placed inside a 60 °C oven overnight for thermal curing. The as-formed PANI thin film is then cooled down to room temperature, and then placed into a deinonized (DI) water bath for 24 hours. After soaked in DI water, the PANI thin film delaminates from the glass substrate. This film is then tap dried with chemwipe and then let it air dried overnight by placing it between two glass substrates to keep it flat. The flat film is then cut into many thin strips (0.1×2.0 cm) for further use.

The surface morphology and the cross section of the films were examined by using a scanning electron microscopy (JEOL 6300 FX). The conductivity of the films was measured by the four-probe method. Mechanical properties of the membranes were measured using Shimadzu EZ-Test equipment. All the measurements were performed on 50.0 mm long and 5.0 mm wide strip that were cut from a large PANI-graphite film. Both ends of the strip were held by the grips of the instrument. The strip was stretched at a constant displacement rate of 1 mm/min, and the stress-strain curve was obtained. Typically, three tests were performed on each membrane. The values reported in this paper are the average of these three trials.

Electrochemical analysis such as cyclic voltammetry and multipotential steps, were carried out in 1.0 M hydrochloric acid with an Autolab PGSTAT30 electrochemical instrument. The cell was set up with platinum electrodes attached to both sides of the PANI thin film coated with polyelectrolyte. Of these two platinum electrodes, one of the them is in direct contact with PANI thin film as working electrode and the other is sit on top of a insulating layer that is adhere to PANI as a counter electrode. The movement of the actuator was monitored by a KEYENCE laser displacement meter. Because PANI does not reflect laser light effectively, a piece of smooth substrate was glue onto the tip of the actuator to reflect laser light. The bending movement was monitored in real time using a KEYENCE laser displacement meter (LDM) with a LK-503 sensor head and an LK-2503 controller with a precision of 10 micrometers. A virtual instrument Lab View program was developed to

control the LDM and to synchronize it with the electrical signal generated by the Autolab electrochemical workstation. The angular displacement of the actuator was measured in real time.

3. RESULTS AND DISCUSSION

3.1 Electrochemical activity of solid-state actuator

The electroactivity of the PANI thin film coated with polyelectrolyte is studied by cyclic voltammetry and the result is shown in Fig. 1. As can be seen from Fig. 1, there are two redox pairs at 0.10V/0.12V and 1.40V/01.25V, respectively. This result is surprisingly consistent with the cyclic voltammogram obtained from PANI thin film in an aqueous solution. The environment provided by the solid-state polyelectrolyte is similar to the aqueous solution. Increasing the scan rate further shifts the redox pairs of the PANI thin film suggest that it is a diffusion dominated process. The above results suggest that the polyelectrolyte system that we used here is effective to offer electrochemical activity of PANI.

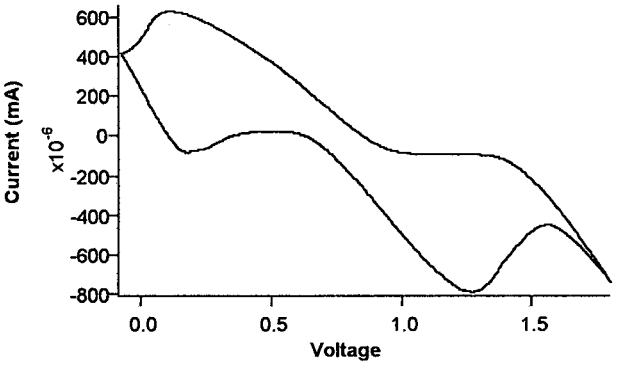

Figure 1 Cyclic voltammogram of solid-state PANI actuator

3.2 Measurements of voltage, current, displacement and bending angle in real time

Once the effectiveness of the polyelectrolyte system is established, we first measure the bending angle and displacement of the solid-state actuator. To better monitor the bending angle using laser displacement meter, a piece of smooth substrate was glue onto the tip of the actuator to reflect laser light. Taking into account that the equilibrium potential of the PANI asymmetric membrane in a 1.0 M HCl aqueous solution is 0.4 V vs. SCE, we

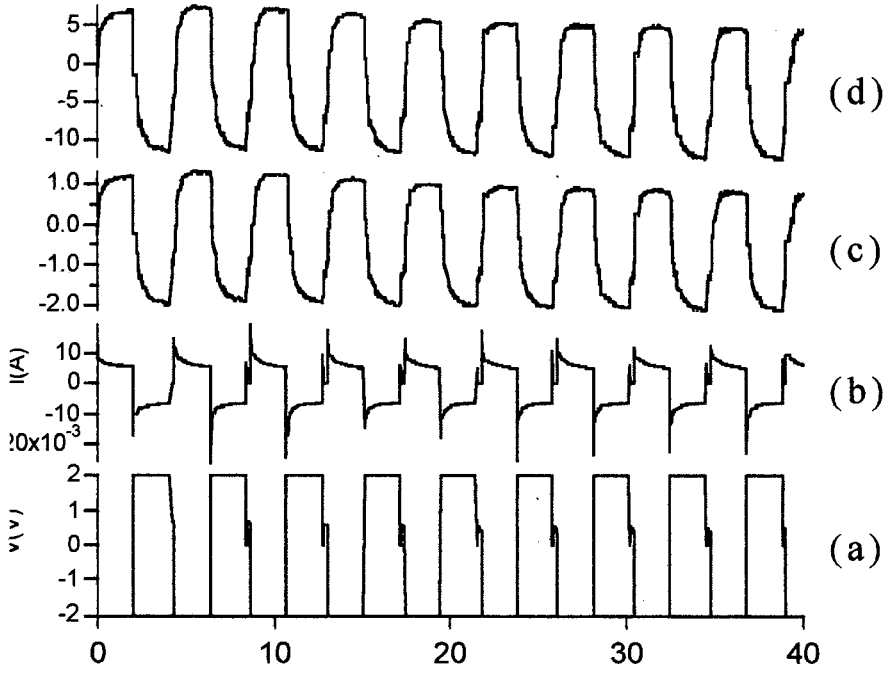

Figure 2 The applied voltage (a), response current (b), resulted displacement(c), and the bending angle(d) for the electrochemical actuator with solid electrolyte under the stimulation of voltage (square wave). Voltage □ 2.00V, frequency 0.25Hz.

performed the potentiostatic characterization of the actuator movement by applying a symmetric square wave potential with an overpotential of +/–2.0 V. Figure 2 shows the plots of voltage, bending angle, current and angular displacement of the electrochemical actuator operated at 0.25 Hz. The bending angle decreases is ~10 degrees and the redox current is ~10 mA. Note that the synchronization between the bending movement of the actuator and the applied electric signal is both strong and stable. Furthermore, the angular displacement of the actuator follows the applied electric signal, and the change in electric polarity dominates the direction of the bending movement. Similar study is carried out under different operating frequencies. As we increase the operating frequencies, the electric charge, bending angle and displacement decreases. The fact that bending angle is charge dependent suggests that the redox current which changes the oxidation states hence the conformation of the polymer chain is likely to be responsible for the volume deformation. Noting that the electrolyte diffuses in and out of the polymer film to maintain charge neutrality as we change the electric field should always be taken into account as a potential driving force for volume expansion/contraction.

3.3 Force measurements in real time

Besides the measurements of current, bending angle and displacement, measurement of force generation is another crucial parameter in deciding the efficiency of the as-prepared PANI actuator. The force generated per unit weight of PANI is also an important data to fully realize the potential of this material as artificial muscle. The apparatus for measuring force generated by the actuator is shown in Fig. 3. The tip of the PANI actuator is attached to the lever arm of the force transducer. As we applied the stimulating signal (a square wave potential) to the actuator, the actuator push the lever arm and the force is recorded in real time. A typical plot of force generation vs. time is shown in Fig. 4. It is important to note that the force transducer only measure the force generated in one direction. The force can't be measured as the PANI actuator pulls the lever arm inward. Consequently, it will appear as a valley in the force vs. time plot. The maximum force generated is determined by the force difference correspond to the peak and the valley (see Fig. 4).

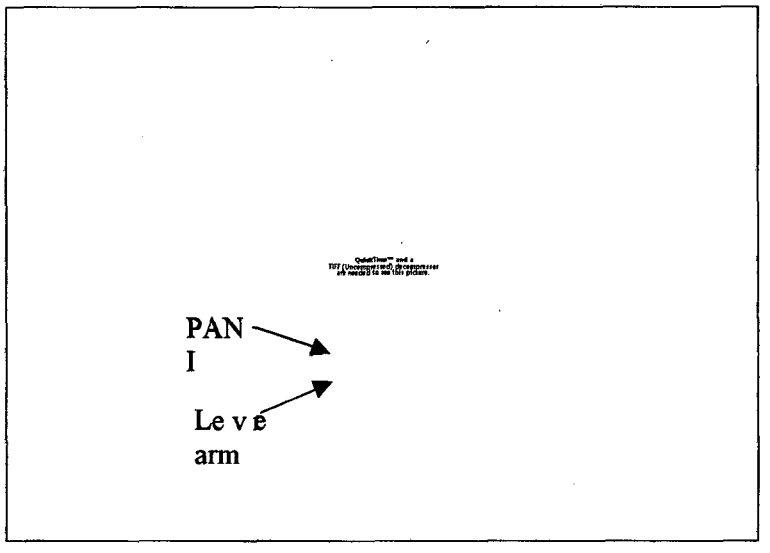

Figure 3 Solid-state PANI actuator attach to the lever arm of a Auora force transducer

3.4 Origin of force generation

In order to better understand the origin of the force generation, we carry out experiments to measure force at three different lengths. After the first force measurement on the actuator of 20 mm length, it was cut into half of its original length (10 mm) and again cut into 5mm. The force generated at different lengths is shown in Fig. 4. As we shortened the length of the actuator, the force generated by the corresponding actuator increases. The force measured for 20 mm, 10 mm and 5 mm actuator is 0.029g, 0.049g, and 0.095g, respectively. Clearly, there is a linear relationship if we plot the length of the actuator vs. the force measured. The overall torque calculated for these three lengths are 5.7×10^{-6} Nm, 4.8×10^{-6} Nm, and 4.7×10^{-6} Nm. All the above results suggest that the force is not generated throughout the whole PANI thin film. We expect the force generate by the actuator to remain constant as we decreasing the length of the actuator if force exerted to push the lever arm is spread homogeneously through out the PANI actuator and we should see decreasing of the overall torque as the length of the actuator decreases. In fact, the above results can be easily explained by a single point force origin which is close to the electric contact between PANI and platinum. This is contrast to the model in which the whole PANI thin film contributed to the total force generated by the actuator. Experimentally, we have observed a bending

movement that only took place near the electric contact and the rest of the film remains perfectly straight. This problem, which was already discussed in our previous paper, is related to a conductivity problem of the PANI membrane.[15] In fact, the voltage distribution along the length of the membrane is not uniform, and the bending only occurs at the very top, therefore the challenge of our future work is to improve the electric conductivity of the PANI thin film to achieve an uniform bending, while still keeping the asymmetric structure along the cross section. We expect the force and work efficiency can be significantly enhanced should the conductivity of the PANI thin film is high enough that homogeneous bending movement throughout the film can be achieved.

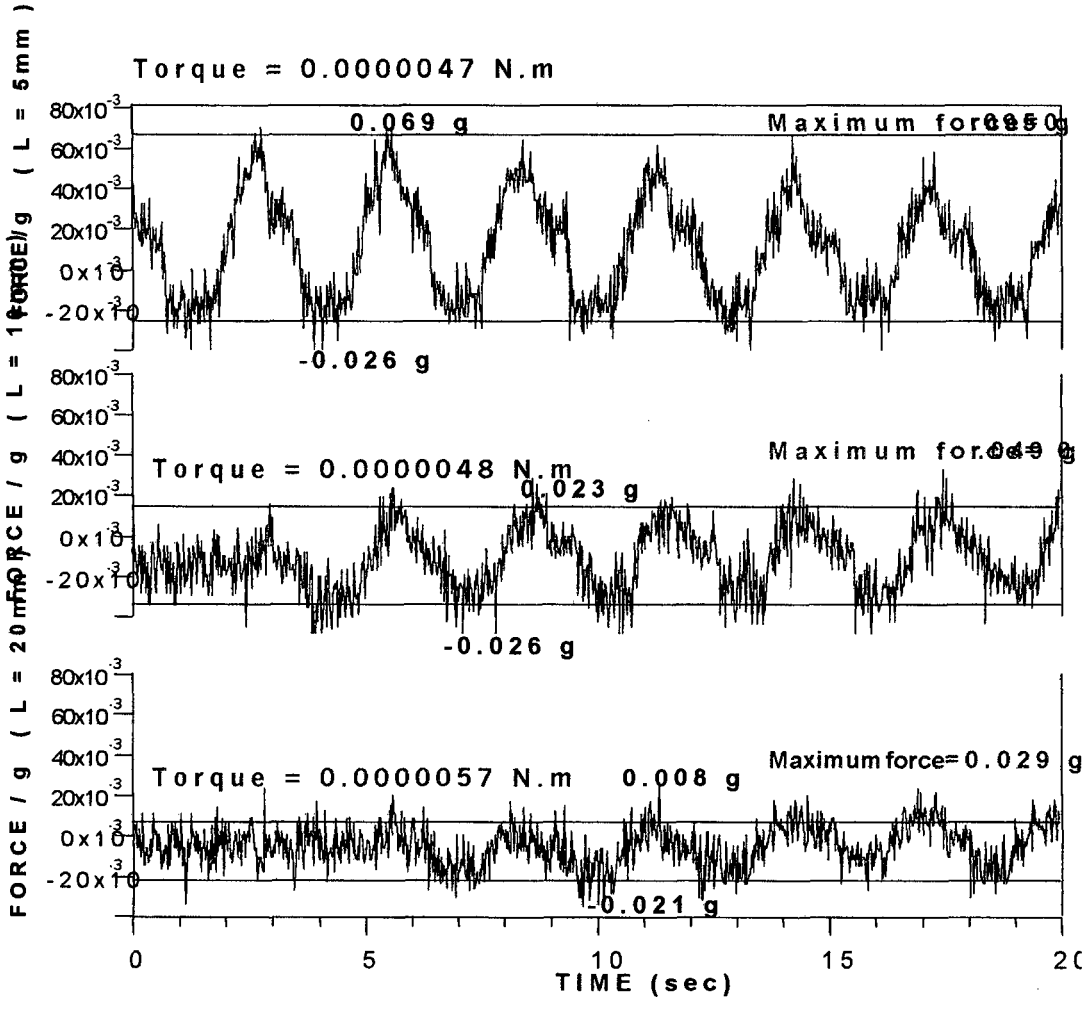

Figure 4 Force generation as a function of the length of the PANI thin film

4. ACKNOWLEDGEMENT

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